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VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.—J. P. COOKE, *Director*.

SILICOTETRAFLUORIDES OF CERTAIN BASES.

BY ARTHUR M. COMEY AND F. W. SMITH.

Presented November 8, 1887.

SUPPLEMENTARY to the investigations* made by C. Loring Jackson and one of us on the action of fluoride of silicon on organic bases, we have further tried the action of fluoride of silicon on nitrosodimethylaniline, pyridine, cinchonine, and quinine.

Trinitrosodimethylaniline disilicotetrafluoride, $(C_8H_{10}N_2O_3)_3(SiF_4)_2$.—This compound was formed by passing fluoride of silicon through a solution of the base in benzol. A lemon-yellow precipitate was formed, which was washed thoroughly with benzol and dried at 100°. The following results were obtained from the analysis of this product:

0.1822 grm. of the substance gave 0.0345 grm. of silicic dioxide and 0.0936 grm. of sodic fluoride.

	Calculated for $(C_8H_{10}N_2O_3)_3(SiF_4)_2$.	Found.
Silicon	8.54	8.83
Fluorine	23.09	23.25

Trinitrosodimethylaniline disilicotetrafluoride is a bright yellow amorphous powder, which is decomposed by water, with separation of silicic dioxide, and decomposes completely with slight explosion when heated above 150°.

Dipyridine silicotetrafluoride, $(C_5H_5N)_2SiF_4$.—This substance was prepared by passing fluoride of silicon through a solution of pyridine in benzol, whereupon it separates out in the form of a heavy voluminous precipitate, which when washed with benzol and dried, and immediately analyzed, gave the following results:

* *Ante*, p. 20.

0.3132 grm. of the substance gave 0.0925 grm. of silicic dioxide and 0.2039 grm. of sodic fluoride.

	Calculated for (C ₅ H ₅ N) ₂ SiF ₄ .	Found.
Silicon	10.77	10.81
Fluorine	29.00	29.45

Dipyridine silicotetrafluoride is a pure white amorphous powder, which decomposes upon standing, giving off pyridine and forming tripyridine disilicotetrafluoride.

Tripyridine disilicotetrafluoride, (C₅H₅N)₃(SiF₄)₂. — This compound is formed by subliming the previous substance. Pyridine is given off and tripyridine disilicotetrafluoride sublimes, forming a crust possessing a distinct crystalline structure. It is extremely deliquescent and was not obtained in a pure state for analysis. The following results of the analysis of the slightly deliquesced substance leave no doubt as to its true constitution.

0.1743 grm. of the substance gave 0.0443 grm. of silicic dioxide and 0.1248 grm. of sodic fluoride.

	Calculated for (C ₅ H ₅ N) ₃ (SiF ₄) ₂ .	Found.
Silicon	12.68	11.86
Fluorine	34.14	32.16

When fluoride of silicon was passed into the ethereal solutions of *cinchonine* or *quinine*, a gummy substance separated, which probably possessed a constitution similar to that of the above substances.

The constitution of these substances has been discussed at length in a previous paper* by C. Loring Jackson and one of us. It remains only to add, that the compounds of which dianiline silicotetrafluoride is the type seem to be formed first. These are very unstable, giving up one molecule of the base with the greatest ease to form compounds corresponding to trianiline disilicotetrafluoride. This extra molecule of the base in most cases is separated by merely washing with a solvent as benzol, as in the case of aniline, toluidine, diphenylamine, chinoline, etc. In others, as dimethylamine and pyridine, the extra molecule is only given off upon standing, or by the action of heat.

Boron trifluoride gave products with organic bases which apparently possess an analogous constitution, but the substances formed were not further investigated.

* *Ante*, p. 32.

According to Schiff,* stannic tetrachloride forms an addition product with aniline, of the composition $(C_6H_7N)_4SnCl_4$. With diphenylamine, however, we obtained by the action of stannic tetrachloride a product, melting at $180-181^\circ$, containing no tin ; chlorine was present in large quantity. The investigation of the action of stannic tetrachloride on organic bases will be continued by one of us.

The above work was done in the Summer School of Chemistry at Harvard College.

* Jahresbericht, 1863, p. 412.